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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

57361-57793

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5

09/424760

INTERNATIONAL APPLICATION NO.
PCT/EP98/03204INTERNATIONAL FILING DATE
29 MAY 1998PRIORITY DATE CLAIMED
30 MAY 1997

TITLE OF INVENTION

METHOD FOR PRODUCING A POROUS CARBON ARTICLE AND AN ARTICLE PRODUCED THEREBY

APPLICANT(S) FOR DO/EO/US Sergey K. GORDEEV, Robert G. AVARBZ, Aleksandr E. KRAVTJIK,
Julia A. KUKUSJKINA, Vasiliy V. SOKOLOV, Tatjana V. MAZAEVA and Alla GRECHINSKAYA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(e)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Preliminary Examination Report (PCT/IPEA/409)
International Search Report (PCT/ISA/210)
Patent Application Data Entry Sheet

U.S. APPLICATION NO. (known, see 37 CFR 1.5)

09/424760

INTERNATIONAL APPLICATION NO. PCT/EP98/03204

ATTORNEY'S DOCKET NUMBER
57361-5779317. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$ 970.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$840.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$760.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**

\$ 840

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☒ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 130

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	23 - 20 =	3	x \$18.00	\$ 54
Independent claims	2 - 3 =	0	x \$78.00	\$

MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00 \$

TOTAL OF ABOVE CALCULATIONS = \$ 1,024Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28). + \$**SUBTOTAL =** \$ 1,024Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)). \$**TOTAL NATIONAL FEE =** \$ 1,024Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + \$**TOTAL FEES ENCLOSED =** \$ 1,024Amount to be
refunded: \$

charged: \$

a. ☒ A check in the amount of \$ 1,024. to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. in the amount of \$ to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required by
37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. 25-0120. A duplicate
copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

November 30, 1999

Young & Thompson
745 South 23rd Street
2nd Floor
Arlington, VA 22202
(703) 521-2297

SIGNATURE

Robert J. Patch
NAME17,355
REGISTRATION NUMBER

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
Sergey K. GORDEEV et al.
Serial No. (unknown)
Filed herewith

METHOD FOR PRODUCING A
POROUS CARBON ARTICLE
AND AN ARTICLE PRODUCED
THEREBY

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to the first Official Action and calculation of the filing fee, please substitute pages 3-7,9 and 15-19 with the attached pages 3-6,6a,7,9,15 and 16, which were filed in the Article 34 amendment of May 19, 1999 and are attached hereto and marked "AMENDED SHEET".

Also substitute Claims 1-24 as originally filed, with Claims 1-23 as filed in the Article 34 amendment of May 19, 1999. The pages containing Claims 1-23 are marked "AMENDED SHEET" and are attached hereto.

Further, please substitute Figures 1-4 of the drawings with the attached sheet containing Figures 1 and 2 and marked "AMENDED SHEET" as per the Article 34 amendment of May 19, 1999.

Following the insertion of claims 1-23, please amend these claims as follows:

09/424760-020300

IN THE CLAIMS:

Claim 3, line 1, change "Claims 1 or 2" to --Claim 1--.

Claim 4, line 1, change "any one of Claims 1-3" to --Claim 1--.

Claim 5, line 1, change "any one of Claims 1-4" to --Claim 1--.

Claim 6, line 1, change "any one of Claims 1-5" to --Claim 1--.

Claim 7, line 1, change "any one of Claims 1-6" to --Claim 1--.

Claim 8, line 1, change "any one of Claims 1-6" to --Claim 1--.

Claim 9, line 1, change "any one of Claims 1-8" to --Claim 1--.

Claim 11, line 1, change "any one of Claims 1-8" to --Claim 1--.

Claim 13, line 1, change "any one of Claims 1-12" to --Claim 1--.

Claim 14, line 1, change "any one of Claims 1-12" to --Claim 1--.

Claim 15, line 1, change "any one of Claims 1-14" to --Claim 1--.

Claim 16, line 1, change "any one of Claims 1-15" to --Claim 1--.

Claim 17, line 1, change "15 or 16" to --1--.

Claim 20, line 1, cancel "or 19".

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Claim 21, line 1, change "Claims 18, 19 or 20" to
--Claim 18--.

Claim 22, line 1, change "Claims 18, 19 or 20" to
--Claim 18--.

Claim 23, line 1, change "any Claims 18-22" to
--Claim 18--.

R E M A R K S

The above changes in the specification, claims and drawings merely place this national phase application in the same condition as it was during Chapter II of the international phase. The multiple dependencies in the claims have been removed and there are now only 23 claims in the case. Figures 3 and 4 of the drawings have been deleted.

Respectfully submitted,

YOUNG & THOMPSON

By



Robert J. Patch
Attorney for Applicants
Registration No. 17,355
745 South 23rd Street
Arlington, VA 22202
Telephone: 703/521-2297

November 30, 1999

SUMMARY OF THE INVENTION

This object is achieved by a method for producing a porous carbon article comprising the steps of formation of one or more carbide powders to an intermediate body with transport pores, i.e. pores having a size larger than 100 nm, by shaping, characterised by the further steps of, selecting the one or more carbide powders on the basis of dependence of specified nanopore size on physical and chemical constants of the carbides using the relationship;

$$X = Z \cdot (1 - R) / R$$

where X = specified size of nanopores, nm;

$$Z = 0.65 - 0.75 \text{ nm};$$

$$R = v M_{CpK} / M_K \rho_C$$

where M_C - molecular mass of carbon, g/mole;

M_K - molecular mass of carbide, g/mole;

ρ_K - density of carbide, g/ccm;

ρ_C - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule,
heat treating the intermediate body in a medium of gaseous hydrocarbon or hydrocarbon mixtures at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons until the mass of the intermediate body has increased at least 3% thereby creating a workpiece in the form of a rigid carbonaceous skeleton,
thereafter thermochemically treating the work piece in a medium of gaseous halogens
to provide predetermined nanopore sizes, i.e the pores have a size less than 10 nm, a predetermined volume of nanopores, and a predetermined distribution of nanopores within the volume of the article, the carbides used forming carbons

5

10 The formulation of carbide particle mixture is chosen in dependence of desired distribution of nanopores by sizes using the relationship;

15

φ_i - volumetric part of i-th carbide in particle mixture;

$$K_i = 1 - v M_{C\rho_{ki}} / M_{ki\rho_C}$$

v - number of carbon atoms in carbide molecule.

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$$\varepsilon_0 = [1 - v_{np} / \sum K_i \phi_i] * 100$$

where ε_0 - porosity of intermediate body, vol%;

ϕ_i - volumetric part of i-th carbide in particle

5 mixture;

v_{np} - predetermined volumetric part of nanopores in
final article;

$$K_i = 1 - v_{M_C} \rho_{ki} / M_{ki} \rho_C ;$$

10

where M_C - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of it-h carbide, g/mole;

ρ_{ki} - density of it-h carbide, g/ccm;

ρ_C - density of carbon, g/ccm;

15 v - number of carbon atoms in carbide molecule.

The treatment in a medium of gaseous hydrocarbon or
hydrocarbon is carried out until the mass of the intermediate
body has changed according to the following relationship;

20

$$\Delta m = Q(\varepsilon_0 - v_{tr}) / (1 - \varepsilon_0)$$

where Δm - relative change of intermediate body mass,
g/g;

25 ε_0 - porosity of intermediate body, vol%;

v_{tr} - predetermined volumetric content of transport
pores, vol%;

$$Q = \rho_C / \rho_{mix}$$

30

Where ρ_C = density of carbon, g/ccm;

ρ_{mix} = density of carbides mixture, g/ccm;

The intermediate body can be formed by pressing. Other well known forming methodes, such as slip casting, tape casting or
5 slurry casting and injection moulding can of course also be used. Natural gas is used as a mixture of hydrocarbons and the treating in hydrocarbon medium is carried out at 750-950° C.

10 Alternatively at least one of the hydrocarbons used during the treatment of the intermediate body in hydrocarbons medium is selected from the group of acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives and the treating in hydrocarbon medium is carried out at 550-1200
15 °C.

The particles of carbide or carbides of which the intermediate body is formed are arranged uniformly or nonuniformly throughout its volume.

20 The thermochemical treatment of the workpiece is carried out in a medium of gaseous halogens at 350-1200°C, preferably chlorine. at 500-1100°C.

25 The present invention relates also to a porous carbon article having nanopores, i.e pores having a size less than 10 nm, and transport pores, i.e. pores having a size grater than 100 nm, characterised in that the article consists of a rigid carbon skeleton in which at least 3 % of its mass consists of
30 carbon without nanopores.

In an embodiment the article has nanopores of at least two sizes. Furthermore, the volume of nanopores is 15-50 % and the volume of transport pores is 10-55 % the nanopores are

BRIEF DESCRIPTION OF THE DRAWING

The present invention will now be described with reference to the following figures, of which;

10

[illegible]

Figs. 2 disclose porosimetry data for the sample of example 1 .

5 DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The method according to the invention comprises the following steps:

- 10 1) Forming a workpiece with transport porosity using particles of a carbide or carbides of elements from III, IV, V and VI groups of Mendeleev's Periodic System, in the form of a rigid carbonaceous skeleton containing in its structure particles of a carbide or carbides selected from the said groups
15 and arranged in a predetermined order providing formation in the subsequent steps desired transport porosity and nanoporosity by sizes, volume and distribution of pores throughout the volume of the article;
- 20 2) Formation of nanoporosity throughout the volume of a workpiece obtained in the 1st step by thermochemical treatment of the said workpiece in gaseous halogens, such as chlorine, at elevated temperatures in the range of 350 to 1200°C, preferably 500-1100°C.

25 Current notions of carbon materials structure point out that nanopores generated during the thermochemical treatment process are formed by ordered or disordered graphite planes of carbon, which for simplicity might be considered as shaped as
30 slots, the width of the latter depending on type of carbide used for forming of the workpiece with transport porosity.

These theoretical ideas are in good agreement with experimental data which allowed the inventors to disclose the following
35 dependence for carbon materials having such structure:

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Under these conditions a decomposition of hydrocarbon occurs by reaction;



with deposition of the generated pyrocarbon on the surface and in the pores of intermediate body volume.

The specified range of initial porosity is based on the fact that at a porosity below 30% it is difficult to obtain sufficient volume of transport pores in the article providing access of adsorptive to nanopores where adsorption process occurs and at a porosity above 70% the article does not possess satisfactory mechanical strength.

The value of 35-50 vol% is preferable because it is easily achieved by any available method of workpiece forming and it assures an optimal relation between volumes of transport pores and nanopores in the article.

The size and distribution of the transport pores can be controlled by selecting appropriate particle sizes and particle distribution. The amount of possible particle packing due to the forming process will of course also influence the porosity of the work piece.

Calculation of concrete value of intermediate body porosity necessary to obtain a predetermined volume of nanopores, is carried out using the following expression:

$$\varepsilon_0 = [1 - v_{np} / \sum_{i=1}^n K_i \varphi_i] \cdot 100 \quad (3)$$

where ε_0 - porosity of intermediate body, vol%;

φ_i - volumetric part of i-th carbide in powder mixture;

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The needed mass change of the intermediate body during pyrocarbon deposition is calculated by formula (4), assuming a transport porosity of 35 vol%

$$\text{Then, } \Delta m = [0.4476(46-35)/(100 - 46)] \cdot 100 = 9.1\%$$

5

A mixture is prepared using 5.01 g of TiC powder with a size of the particles of 20 μm . Ethyl alcohol is added in the amount of 10% of the mass of the mixture. Then, an intermediate body is formed by pressing on a hydrostatic press machine (P-125) at 30 ± 1 Mpa pressure. After the pressing, the intermediate body is dried at $150 \pm 10^\circ\text{C}$ during 1-1.5 hour until complete removal of temporary binder.

15 This is followed by pyrocarbon deposition on the intermediate body by means of heat treatment in natural gas medium at atmospheric pressure in a quartz continuous reactor at 850°C during 12 hours until change of mass by 9.1%.

20 Then, the sample is chlorinated. The chlorination is carried out in a isothermal quartz reactor at 650°C during 4 hours. Then a blow-through of the reactor with argon at a temperature of 800°C is carried out to remove excessive chlorine out of the reactor zone and the internal surface of the sample.

25

Properties of the obtained material are presented in Table 1. From this table it is evident that the measured peak value of the nanopore size measured by gas porosimetry correspond to the calculated value.

30

Two articles produced according to Example 1 were saturated with 20% KOH solution by boiling and placing them in an electrolyte solution (20% KOH). Opposite by sign potential was applied to each of the articles to form a double electric layer in the material nanopore volume. In this case the spe-

35

cific electrical capacitance of the double electric layer formed in the material was 37.8 F/g.

Notes:

- 1) Total volume of pores is determined by hydrostatic method according to GOST 473.4-81.
- 2) Nanopore volume is determined by exsiccator method by adsorption of benzene under static conditions, see "Fundamentals of adsorption technology." Keltsev N.V., Moscow, Chemistry publishers, 1984, p. 33.
- 3) Transport pore volume is determined by formula

$$V_{tr} = V_T - V_{np}.$$

- 4) Size of nanopores is determined by means of mercury and gas porosimetry (Micromeretics Auto Pore III and Micromeretics ASAP 2010, respectively). Data are shown in Figures 2-4. Legend Hg denotes mercury porosimetry intrusion data, legend BJH denotes gas porosimetry desorption data analysed by the BJH method, and legend Micro denotes gas porosimetry data analysed by the Horvath-Kawazoe method.

The presented data allows one to draw the conclusion that a new method for producing a porous carbon article comprising transport pores and nanopores with controllable sizes and distribution of nanopores throughout its volume as well as

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CLAIMS (amended)

1. A method for producing a porous carbon article comprising the steps of formation of one or more carbide powders to an intermediate body with transport pores, i.e. pores having a size larger than 100 nm, by shaping, **characterised** by the further steps of, selecting the one or more carbide powders on the basis of dependence of specified nanopore size on physical and chemical constants of the carbides using the relationship;

$$X = Z \cdot (1 - R) / R$$

where X = specified size of nanopores, nm;

$$Z = 0.65 - 0.75 \text{ nm};$$

$$R = v M_c \rho_k / M_k \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_k - molecular mass of carbide, g/mole;

ρ_k - density of carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule,

- heat treating the intermediate body in a medium of gaseous hydrocarbon or hydrocarbon mixtures at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons until the mass of the intermediate body has increased at least 3% thereby creating a workpiece in the form of a rigid carbonaceous skeleton, thereafter thermochemically treating the work piece in a medium of gaseous halogens to provide predetermined nanopore sizes, i.e the pores have a size less than 10 nm, a predetermined volume of nanopores, and a predetermined distribution of nanopores within the volume of the article, the carbides used forming carbons having a slot-like structure

2. A method according to Claim 1, **characterised** in that elements from III, IV, V or VI group of Mendeleyv's Periodic system are selected as carbon precursor.

3. A method according to Claims 1 or 2, characterised in that the formulation of carbide particle mixture is chosen in dependence of desired distribution of nanopores by sizes using the relationship;

$$\Psi_i = K_i \varphi_i / \sum K_i \varphi_i$$

where Ψ_i - volumetric part of nanopores with size x_i in total volume of nanopores;
 φ_i - volumetric part of i-th carbide in particle mixture;
 n - number of carbides;

10

$$K_i = 1 - v M_c \rho_{ki} / M_{ki} \rho_c$$

where M_c - molecular mass of carbon, g/mole;
 M_{ki} - molecular mass of i-th carbide, g/mole;
 ρ_{ki} - density of i-th carbide, g/ccm;
 ρ_c - density of carbon, g/ccm;
 v - number of carbon atoms in carbide molecule.

15

4. A method according to any one of Claims 1-3, characterised in that the intermediate body is formed with a porosity of 30-70 vol%, preferably 35-50 vol%.

20

5. A method according to any one of Claims 1-4, characterised in that the intermediate body is formed with a porosity determined with the following relationship;

$$\varepsilon_0 = [1 - v_{np} / \sum K_i \varphi_i] * 100$$

25

where ε_0 - porosity of intermediate body, vol%;
 φ_i - volumetric part of i-th carbide in particle mixture;
 v_{np} - predetermined volumetric part of nanopores in final article;

30

$$K_i = 1 - v M_c \rho_{ki} / M_{ki} \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of it-h carbide, g/mole;

ρ_{ki} - density of it-h carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule.

5

6. A method according to any one of Claims 1-5, characterised in that the treatment in a medium of gaseous hydrocarbon or hydrocarbon is carried out until the mass of the intermediate body has changed according to the following relationship;

10

$$\Delta m = Q(\varepsilon_0 - v_{tr}) / (1 - \varepsilon_0)$$

where Δm - relative change of intermediate body mass, g/g;

ε_0 - porosity of intermediate body, vol%;

v_{tr} - predetermined volumetric content of transport pores, vol%;

15

$$Q = \rho_c / \rho_{mix}$$

Where ρ_c = density of carbon, g/ccm;

ρ_{mix} = density of carbides mixture, g/ccm;

20

7. A method according to any one of Claims 1-6, characterised in that the intermediate body is formed by pressing.

8. A method according to any one of Claims 1-6, characterised in that the intermediate body is formed by slip casting, tape casting or slurry casting.

25

9. A method according to any one of Claims 1-8, characterised in that natural gas is used as a mixture of hydrocarbons.

10. A method according to Claim 9, characterised in that the treating in hydrocarbon medium is carried out at 750-950°C.

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11. A method according to any one of Claims 1-8, **characterised** in that at least one of the hydrocarbons used during the treatment of the intermediate body in hydrocarbons medium is selected from the group of acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives.

5

12. A method according to Claim 11, **characterised** in that the treating in hydrocarbon medium is carried out at 550-1200°C.

10 13. A method according to any one of Claims 1-12, **characterised** in that the particles of carbide or carbides of which the intermediate body is formed are arranged uniformly throughout its volume.

15 14. A method according to any one of Claims 1-12, **characterised** in that the particles of carbide or carbides of which the intermediate body is formed are arranged non-uniformly throughout its volume.

20 15. A method according to any one of Claims 1-14, **characterised** in that the thermochemical treatment of the workpiece is carried out in a medium of gaseous halogens, such as chlorine.

25 16. A method according to any one of Claims 1-15, **characterised** in that the thermochemical treatment of the workpiece is carried out at 350-1200°C.

30 17. A method according to claim 15 or 16, **characterised** in that chlorine is preferably used for the thermochemical treatment at 500-1100°C.

18. A porous carbon article having nanopores, i.e pores having a size less than 10 nm, and transport pores, i.e. pores having a size greater than 100 nm, **characterised** in that the article consists of a rigid carbon skeleton in which at least 3 % of its mass consists of carbon without nanopores.

19. A porous carbon article according to Claim 18, **characterised** in that it has nanopores of at least two sizes.

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20. An article according to Claim 18 or 19, characterised in that the the volume of nanopores is 15-50 % and the volume of transport pores is 10-55 %

5 21. An article according to Claims 18,19 or 20, characterised in that the nanopores are distributed uniformly throughout the volume of the article.

22. An article according to Claims 18,19 or 20, characterised in that the nanopores are distributed nonuniformly throughout the volume of the article.

10 23. An article according to any Claims 18- 22, characterised in having a specific electrical capacitance of at least 30 F/g when used as electrode material in a double electric layer capacitor.

15

Table 1

Ex No	Carbide mixture composition (wt%)	Total volume of pores ¹⁾ , V_{tot} (cc/cc)	Nanopore volume, ²⁾ , V_{np} (cc/cc)	Transport pore volume ³⁾ , V_{tr} (cc/cc)	Size of pores, calculated ⁴⁾ (nm)		Size of pores, measured ⁵⁾ (nm)	
					X_1	X_2	X_1	X_2
1	100% TiC	0,67	0,32	0,35	0,8 - 0,92		0.8	

FIG. 1

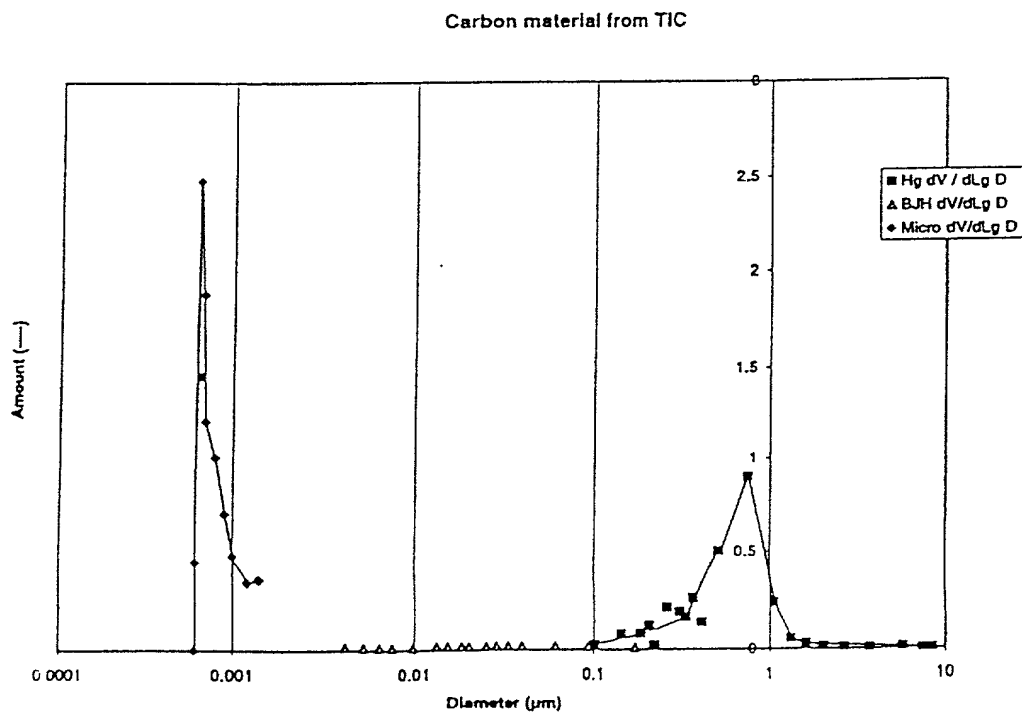


FIG. 2

A METHOD FOR PRODUCING A POROUS CARBON ARTICLE AND AN ARTICLE
PRODUCED THEREBY

TECHNICAL FIELD

5 The present invention relates to a method for producing a porous carbon article comprising the steps of forming a workpiece with transport porosity and forming nanopores in said workpiece by thermochemical treatment. The invention also
10 relates to an article produced by said method.

BACKGROUND TO THE INVENTION

From "Application of tubular articles in cryoadsorption
15 pumps//Carbon adsorbents and their application in industries.", Breslavets K.S et al, Moscow, Science publishers, 1983, p. 243, a method for producing a porous carbon article is known. The method comprises a step of forming or extrusion
20 of a paste consisting of silicon carbide powder and commercial synthetic resins as a binder in order to produce a desired article. In this case, transport porosity of the material is formed with pore size above 100 nm. Then a carbonization in an inert medium is carried out in order to strengthen the article and make its structure more uniform. Further the
25 article undergoes a thermochemical treatment by chlorine at 900 - 1000°C for transformation of carbide into carbon. In this step, in the volume of the article a nanoporous structure with pore size less than 10 nm is formed.

30 Use of a polymeric resin as a binder is an obstacle for obtaining high mechanical strength, because of the low mechanical strength of carbonized resin. Resin destruction accompanies formation of carbon which also takes part in the process of forming nanoporosity, but the size of this porosity is
35 practically uncontrollable. As a result, it is impossible to produce materials with predetermined adsorption properties with the known method.

An article produced by means of the known method is a carbon material binded with products of resin carbonization with porosity of 65 to 75 vol%. In this case, a part of the pores, 30-32 vol% are transport pores having size greater than 100 nm, while other pores have size less than 10 nm.

Application of articles obtained by the known method is restricted because it gives no possibility to obtain controllable size of pores as well as controllable volumetric content of both transport porosity and nanoporosity.

A number of so called activated carbons with a high content of nanoporosity is known, but the pore size distribution for these materials is very wide and uncontrolled, c.f. "Carbon", John Wiley & Son, N.Y. 1988, USA.

It is thus a need for a method in which the porosities of a porous carbon material which comprise two types of pores can be controlled. The two types are pores of a size less than 10 nm providing adsorption ability and pores of a size greater than 100 nm providing transportation of a component to the pores taking active part in the adsorption process. Articles produced by such a method can be used in different fields of technology connected with adsorption and absorption processes, such as selective absorption of a component from a liquid or gas, electrochemical electrodes, in medicine technologies, etc.

The object of the present invention is to make it possible to produce carbon porous articles with predetermined transport porosity and predetermined nanopore sizes, volume and distribution throughout the volume of the article.

SUMMARY OF THE INVENTION

This object is achieved by a method for producing a porous carbon article comprising the steps of formation of one or more carbide powders to an intermediate body with transport pores, i.e. pores having a size larger than 100 nm, by shaping, characterised by the further steps of, selecting the one or more carbide powders on the basis of dependence of specified nanopore size on physical and chemical constants of the carbides using the relationship;

$$X = Z \cdot (1 - R) / R$$

where X = specified size of nanopores, nm;

$$Z = 0.65 - 0.75 \text{ nm};$$

$$R = v M_C \rho_K / M_K \rho_C$$

where M_C - molecular mass of carbon, g/mole;

M_K - molecular mass of carbide, g/mole;

ρ_K - density of carbide, g/ccm;

ρ_C - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule,
heat treating the intermediate body in a medium of gaseous hydrocarbon or hydrocarbon mixtures at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons until the mass of the intermediate body has increased at least 3% thereby creating a workpiece in the form of a rigid carbonaceous skeleton,
thereafter thermochemically treating the work piece in a medium of gaseous halogens
to provide predetermined nanopore sizes, i.e the pores have a size less than 10 nm, a predetermined volume of nanopores, and a predetermined distribution of nanopores within the volume of the article, the carbides used forming carbons

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20 n - number of carbides;

$$\varepsilon_0 = [1 - v_{np} / \sum K_i \phi_i] * 100$$

where ε_0 - porosity of intermediate body, vol%;

ϕ_i - volumetric part of i-th carbide in particle

5 mixture;

v_{np} - predetermined volumetric part of nanopores in final article;

$$K_i = 1 - v_{M_C} \rho_{k_i} / M_{k_i} \rho_C$$

10

where M_C - molecular mass of carbon, g/mole;

M_{k_i} - molecular mass of it-h carbide, g/mole;

ρ_{k_i} - density of it-h carbide, g/ccm;

ρ_C - density of carbon, g/ccm;

15 v - number of carbon atoms in carbide molecule.

The treatment in a medium of gaseous hydrocarbon or hydrocarbon is carried out until the mass of the intermediate body has changed according to the following relationship;

20

$$\Delta m = Q(\varepsilon_0 - v_{tr}) / (1 - \varepsilon_0)$$

where Δm - relative change of intermediate body mass, g/g;

25 ε_0 - porosity of intermediate body, vol%;

v_{tr} - predetermined volumetric content of transport pores, vol%;

$$Q = \rho_C / \rho_{mix}$$

30

Where ρ_C = density of carbon, g/ccm;

ρ_{mix} = density of carbides mixture, g/ccm;

The intermediate body can be formed by pressing. Other well known forming methods, such as slip casting, tape casting or slurry casting and injection moulding can of course also be used. Natural gas is used as a mixture of hydrocarbons and the treating in hydrocarbon medium is carried out at 750-950° C.

10 Alternatively at least one of the hydrocarbons used during
the treatment of the intermediate body in hydrocarbons medium
is selected from the group of acetylene, methane, ethane,
propane, pentane, hexane, benzene and their derivatives and
the treating in hydrocarbon medium is carried out at 550-1200
15 °C.

The particles of carbide or carbides of which the intermediate body is formed are arranged uniformly or nonuniformly throughout its volume.

20 The thermochemical treatment of the workpiece is carried out in a medium of gaseous halogens at 350-1200°C, preferably chlorine. at 500-1100°C.

25 The present invention relates also to a porous carbon article
having nanopores, i.e pores having a size less than 10 nm,
and transport pores, i.e. pores having a size greater than 100
nm, characterised in that the article consists of a rigid
carbon skeleton in which at least 3 % of its mass consists of
30 carbon without nanopores.

In an embodiment the article has nanopores of at least two sizes. Furthermore, the volume of nanopores is 15-50 % and the volume of transport pores is 10-55 % the nanopores are

BRIEF DESCRIPTION OF THE DRAWING

The present invention will now be described with reference to the following figures, of which;

Fig.1 shows a table of the properties of materials produced
10 in example 1, and

Abstract

Figs. 2 disclose porosimetry data for the samples of examples 1.

5 DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The method according to the invention comprises the following steps:

- 1) Forming a workpiece with transport porosity using particles of a carbide or carbides of elements from III, IV, V and VI groups of Mendeleev's Periodic System, in the form of a rigid carbonaceous skeleton containing in its structure particles of a carbide or carbides selected from the said groups and arranged in a predetermined order providing formation in the subsequent steps desired transport porosity and nanoporosity by sizes, volume and distribution of pores throughout the volume of the article;
- 2) Formation of nanoporosity throughout the volume of a workpiece obtained in the 1st step by thermochemical treatment of the said workpiece in gaseous halogens, such as chlorine, at elevated temperatures in the range of 350 to 1200°C, preferably 500-1100°C.

Current notions of carbon materials structure point out that nanopores generated during the thermochemical treatment process are formed by ordered or disordered graphite planes of carbon, which for simplicity might be considered as shaped as slots, the width of the latter depending on type of carbide used for forming of the workpiece with transport porosity.

These theoretical ideas are in good agreement with experimental data which allowed the inventors to disclose the following dependence for carbon materials having such structure:

$$X = Z \cdot (1-R) / R \quad (1)$$

where X-predetermined size of nanopores, nm;

- 5 Z - experimental factor established for a number of carbide structures of elements from III, IV, V and VI groups of Mendeleev's Periodic System as 0.65-0.75 nm;

$$R = vM_c\rho_k / M_k\rho_c$$

10 where M_c - molecular mass of carbon, g/mole;

M_k - molecular mass of carbide, g/mole;

ρ_k - density of carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

15 v - number of carbon atoms in carbide molecule.

A series of preliminary experiments made it possible to choose a necessary carbide to obtain in practice a predetermined size of nanopores.

20 Particles of a chosen carbide (powder) are formed into an intermediate body with porosity in the range of 30-70 vol% by any known method, e.g. by pressing with or without temporary binder, slip casting, slurry casting. Final step of forming, 25 which results in production of a workpiece with a high mechanical strength and a desired transport porosity, is a treating of the intermediate body in a medium of gaseous hydrocarbon or hydrocarbons mixture at a temperature above their decomposition temperature.

30 It is possible to use natural gas and/or at least a hydrocarbon selected from the group comprising acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives.

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Under these conditions a decomposition of hydrocarbon occurs by reaction;



with deposition of the generated pyrocarbon on the surface and in the pores of intermediate body volume.

The specified range of initial porosity is based on the fact that at a porosity below 30% it is difficult to obtain sufficient volume of transport pores in the article providing access of adsorptive to nanopores where adsorption process occurs and at a porosity above 70% the article does not possess satisfactory mechanical strength.

The value of 35-50 vol% is preferable because it is easily achieved by any available method of workpiece forming and it assures an optimal relation between volumes of transport pores and nanopores in the article.

The size and distribution of the transport pores can be controlled by selecting appropriate particle sizes and particle distribution. The amount of possible particle packing due to the forming process will of course also influence the porosity of the work piece.

Calculation of concrete value of intermediate body porosity necessary to obtain a predetermined volume of nanopores, is carried out using the following expression:

$$\varepsilon_0 = [1 - v_{np} / \sum_{i=1}^n K_i \varphi_i] \cdot 100 \quad (3)$$

where ε_0 - porosity of intermediate body, vol%;

φ_i - volumetric part of i-th carbide in powder mixture;

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V_{np} - predetermined volumetric part of nanopores in final article.

$$K_i = 1 - vM_c\rho_{ki}/M_{ki}\rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of i-th carbide, g/mole;

ρ_c - density of carbon, g/ccm;

ρ_{ki} - density of i-th carbide, g/ccm;

v - number of carbon atoms in carbide molecule;

n - number of carbides in the mixture.

Duration of treating in the said medium is controlled by measuring the mass of the article. When the mass has changed by at least 3%, the strength is already sufficient for use of the article as adsorption element, capacitor electrode or chromatography membrane, for instance.

The process is usually completed when the mass is changed by 3-20%, thus providing necessary strength of the article and its transport porosity. Lower and upper limits are determined by use of carbides from said groups with different densities.

In practice an experimental expression is used allowing for a given type of carbide at predetermined strength properties to obtain necessary value of transport porosity which, depending on active agent in the pores, can determine kinetics of the process. This expression is as follows:

$$\Delta m = Q (\varepsilon_0 - V_{tr}) / (1 - \varepsilon_0); \quad (4)$$

where Δm - relative change of intermediate body mass, g/g;

ε_0 - porosity of intermediate body, vol%;

V_{tr} - predetermined volumetric content of transport pores, vol%;

$$Q = \rho_c / \rho_{\text{mix}}$$

where ρ_c - density of carbon, g/ccm:

ρ_{mix} - density of carbides mixture, g/ccm.

In order to obtain an article with nanopores of different sizes, making it possible to realize selective filtration and adsorption, more than one carbide should be chosen. For this goal the formula (1) or an experimentally determined pore size value is used and the following dependence, confirmed experimentally, allows an determination of the part of each carbide in the mixture necessary to manufacture such an article;

$$\Psi_i = K_i \varphi_i / \sum_{i=1}^n K_i \varphi_i \quad (5)$$

where Ψ_i - volumetric part of nanopores with size X_i in total volume of nanopores;

φ_i - volumetric part of i-th carbide in powder mixture;

n - number of carbides;

$$K_i = 1 - v M_c \rho_{k_i} / M_{k_i} \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{k_i} - molecular mass of i-th carbide, g/mole;

ρ_{k_i} - density of i-th carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

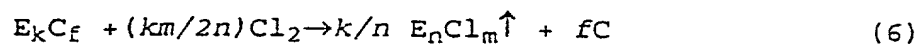
v - number of carbon atoms in carbide molecule.

In order to obtain a uniform distribution of nanopores throughout the article volume a mixture is formed with uniformly distributed powders of various carbides in it (homogeneous mixture); if it is necessary to obtain nanopores distributed throughout the volume in a desired order a mix-

ture is prepared by means of any known method with particles distributed according to the desired order, e.g. layerwise.

After completed forming, a workpiece is obtained as a rigid carbonaceous skeleton with transport porosity formed in its volume allowing to obtain in the step of thermochemical treatment uniform nanopores of a predetermined size.

In order to form nanoporosity the obtained workpiece is subjected to thermochemical treatment by chlorine at 500-1100°C. Nanoporosity is formed at removal of volatile chlorides of carbide-forming elements in accordance with reaction:



where $E_k C_f$ - primary carbide;

k, f, n, m - stoichiometric coefficients.

The treatment is carried out until mass change of the workpiece has stopped.

A finished article produced by the described method has a predetermined shape and size, and its structure is a porous carbon skeleton with transport porosity of 10-55% obtained in the step of forming and nanoporosity of 15-50% volume. The article comprises one or several types of nanopores and each type is being characterized with narrow distribution by size. Carbon content in the skeleton is more than 95 wt%, preferably 99 wt%, i.e., practically, the obtained article consists of pure carbon and has considerable strength allowing to increase its life time and expand application range under conditions when shape maintaining during operation is necessary.

As a result of selecting appropriate carbides and accomplishment of forming under conditions determined beforehand by means of relationships established by the inventors, a fin-

ished article is obtained with nanopore sizes, volume and distribution corresponding to those of the object of the article operation.

- 5 Among possible forming methods to realize the said method pressing, slip casting, tape casting and slurry casting can be named.

10 A formed intermediate body is treated in a medium of at least one hydrocarbon selected from the group comprising acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives. When using hydrocarbons from the said group an optimal temperature range is 550-1200°C, the decomposition
15 temperatures for these hydrocarbons falling within this range. It is also possible to use natural gas and in this case it is expedient to keep temperature in the range of 750-950°C.

20 A halogenation is carried out just like in the known method, with the temperature being selected in the range of 350-1200°C, depending on the nature of initial carbides and the formed volatile halogenides. Under these conditions volatile halogenides of carbide-forming elements are completely removed out of the article according to a reaction similar to
25 reaction (6). However, only halogens and halogenides which do not react with carbon under the prevailing temperature conditions may be used.

30 The claimed concept is further elucidated with the following examples.

Example 1.

35 An example of producing an article in the tablet form with sizes $d = 20$ mm, $h = 5$ mm, with nanopore size 0.8 nm and nanopore volume 0.3 ccm/ccm uniformly distributed throughout the article volume, suitable for forming on its surface a

double electric layer of high capacitance in electrolyte solutions.

To produce an article on the basis of beforehand obtained dependence (1) for $X = 0.8$ nm titanium carbide powder was chosen. By substitution of the values of molecular mass and density of titanium carbide and carbon ($M_c = 12$ g/mole; $\rho_c = 2.2$ g/ccm; $\rho_k = \rho_{TiC} = 4.92$ g/ccm; $M_k = M_{TiC} = 59.88$ g/mole) in the formula (1) the following is obtained:

$$R = 12 \cdot 4.92 / 59.88 \cdot 2.2 = 0.448, \quad X = Z(1 - 0.448) / 0.448 = 1.232Z \text{ nm};$$

Thus when Z is in the range of 0.65-0.75, the nanopore size of the produced carbon materials will be in the range of 0.8-0.92.

In order to obtain the predetermined volume of nanopores ($V_{np} = 0.3$ ccm/ccm), prior to pressing a needed porosity of the intermediate body is determined by the relationship (3):

where $\varphi_i = 1$, $n = 1$, as follows

$$\varepsilon_0 = [1 - 0.3 / (1 - 0.448)] \cdot 100 = 46\%$$

Amount of TiC powder necessary to produce an intermediate body which has the predetermined sizes and the obtained value of porosity is calculated by the following dependence:

$$m = \rho_k (100 - \varepsilon_0) \cdot V / 100$$

where V - article volume, $V = (\pi d^2 / 4) \cdot h$, ccm;

d - workpiece diameter, 2 cm;

h - workpiece height, 0.5 cm;

hence:

$$m = 4.92(100 - 46)(3.14 \cdot 2^2 / 4) \cdot 0.5 = 5.01g$$

Then, $\Delta m = [0.4476(46-35) / (100 - 46)] \cdot 100 = 9.1\%$

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cific electrical capacitance of the double electric layer formed in the material was 37.8 F/g.

~~Example 2.~~

The example of producing an article in a tablet form of $d=30$ mm, $h=3$ mm with a nanopore volume 0.4 ccm/ccm uniformly distributed throughout the article volume suitable for adsorption of organic substances out of a powder of Mo_2C was chosen.

In order to produce the predetermined nanopore volume ($v_{np}=0.4$ ccm/ccm) before pressing the needed porosity of the intermediate body was calculated using expression (3), where $M_{\text{Mo}_2\text{C}}=203,88$ g/mole; $\rho_{\text{Mo}_2\text{C}}=8.91$ g/ccm, $R=0.238$; $\phi_1=1$, $n=1$, as follows: $\varepsilon_0=48\%$

The amount of molybden carbide powder necessary to produce the intermediate body having the predetermined porosity was calculated as in Example 1. In this case the powder article weight was calculated to: $m=9.82$ g

The needed mass change of the workpiece during pyrocarbon deposition was calculated by formula (4), assuming a transport porosity of 40vol%, to $\Delta m=3.8\%$.

Mixture preparation, pyrocarbon deposition and chlorination were carried out as in Example 1.

Properties of the obtained material are presented in Table 1. From this table it is evident that the calculated nanopore size of 1.95-2.25 nm differs from the measured peak value according to figures 3 and 4 which was 3.5 nm. This indicates that Mo_2C probably does not follow the model structure for dependence (1)

The produced article was placed in an exsiccator containing isooctane vapours and was kept there during 24 hours. Then, the article was weighed to determine the amount of adsorbed isooctane, which was 0.95 ccm/g.

Example 3.

An example of producing an article of diameter 30 mm and height 5 mm with nanopores of calculated size 0.8 nm and 2.1 nm uniformly distributed throughout the article volume. In order to obtain the article on the basis of beforehand obtained dependence (1) for $X_1 = 0.8$ nm titanium carbide powder was chosen, for $X_2 = 3.5$ nm - molybdenum carbide powder in accordance with the measured value in Example 2.

In order to provide equal volumetric content of both sizes nanopores a mixture is used containing 40 vol% molybdenum carbide and 60 vol% titanium carbide, that is determined by formula (5). The needed amount of these carbides is calculated as follows:

$$\rho_{\text{mix}} = \varphi_1 \cdot \rho_1 + \varphi_2 \cdot \rho_2$$

where φ_1, φ_2 - volumetric content of titanium carbide and molybdenum carbide, correspondingly $\varphi_1 = 0.4$, $\varphi_2 = 0.6$;

ρ_1, ρ_2 - density of titanium carbide and molybdenum carbide, correspondingly ($\rho_1 = 8.91$ g/ccm, $\rho_2 = 4.92$ g/ccm);

hence $\rho_{\text{mix}} = 0.4 \cdot 8.91 + 0.6 \cdot 4.92 = 6.52$ g/ccm,

hence mass part of molybdenum carbide:

$$\alpha_1 = 0.4 \cdot 8.91 / 6.52 = 0.55 \text{ wt.fraction;}$$

of titanium carbide

$$\alpha_2 = 0.6 \cdot 4.92 / 6.52 = 0.45 \text{ wt. fraction}$$

The mixture is prepared and pressed under conditions of Example 1.

In order to obtain an article of the specified shape and sizes a weight should be calculated according to the following dependence:

$$m = \rho_{\text{mix}}(100 - \epsilon_0) \cdot V / 100$$

where ρ_{mix} - density of carbide mixture;

ϵ_0 - porosity of intermediate body; %vol;

V - article volume, ccm;

d - article diameter, 3 cm;

h - article height, 0.5 cm.

The needed porosity of an intermediate body is chosen according to relation (3).

By substitution of the said values at specified total volume of nanopores 0.4 ccm/ccm we obtain

$$\epsilon_0 = [100 - 0.4 / [(1 - 12 \cdot 8.91 / 2.2 \cdot 203.88) 0.4 + (1 - 12 \cdot 4.92 / 2.2 \cdot 59.88) 0.6]] 100 \approx 37 \text{ vol\%}$$

hence necessary mass of the weight:

$$m = 6.52(100 - 37) \cdot (3.14 \cdot 5^2 / 4) \cdot 0.2 / 100 = 16.1 \text{ g}$$

The obtained intermediate body is heat treated under conditions of Example 1. Introduction of pyrocarbon is carried out under conditions of Example 1 until change of article mass by 7% which is determined by formula (4) under condition:

$$V_{\text{tr}} = 20 \text{ vol\%}$$

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$$\Delta m = 0.337(37-20)/(100 - 37) \cdot 100 = 9.1\%$$

Chlorination of the obtained workpiece is carried out under conditions of Example 1.

Properties of samples produced in Examples 1 - 3 are presented in Table 1. From Table 1 it seems as Mo₂C results in a different carbon nanopore structure than TiC.

The produced article was placed in an exsiccator containing vapours of carbontetrachloride and was kept there during 24 hours. Then the article was weighed to determine the amount of absorbed carbontetrachloride which was 0.61 ccm/g.

Notes:

1) Total volume of pores is determined by hydrostatic method according to GOST 473.4-81.

2) Nanopore volume is determined by exsiccator method by adsorption of benzene under static conditions, see "Fundamentals of adsorption technology." Keltsev N.V., Moscow, Chemistry publishers, 1984, p. 33.

3) Transport pore volume is determined by formula

$$V_{tr} = V_L - V_{np}.$$

4) Size of nanopores is determined by means of mercury and gas porosimetry (Micromeretics Auto Pore III and Micromeretics ASAP 2010, respectively). Data are shown in Figures 2-4. Legend Hg denotes mercury porosimetry intrusion data, legend BJH denotes gas porosimetry desorption data analysed by the BJH method, and legend Micro denotes gas porosimetry data analysed by the Horvath-Kawazoe method.

The presented data allows one to draw the conclusion that a new method for producing a porous carbon article comprising transport pores and nanopores with controllable sizes and distribution of nanopores throughout its volume as well as

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volumetric content of both types of porosity has been developed. The articles according to the invention can find wide application for adsorption and microdosage of substances, purification and separation of cryogenic liquids and gas mixtures, as high-porous electrode materials etc. owing to presence of porosity of desired sizes.

By the inventive method it is possible to produce nanopore volume and size or sizes by a mechanism independent from the mechanism for producing transport porosity in the materials produced, thereby making it possible to control purposely parameters of their porous structure. At development of adsorption materials, for instance, the following parameters can be optimized when using the present invention:

- 1) adaptability to manufacture of devices working components made of these materials;
- 2) optimal relationship between volumes of transport pores and nanopores which provide effective adsorption;
- 3) mechanical strength;
- 4) increased heat conductivity allowing to use these materials in cryo-adsorption evacuation elements.

Furthermore, the present method, besides the advantages pointed out, allows production of articles of complex shapes, in particular, of shapes impossible to obtain by any other known method, with minimum machining required. Owing to high mechanical strength the articles according to the invention can be used under conditions demanding maintenance of their shape.

CLAIMS (amended)

1. A method for producing a porous carbon article comprising the steps of formation of one or more carbide powders to an intermediate body with transport pores, i.e. pores having a size larger than 100 nm, by shaping, **characterised** by the further steps of,
 5 selecting the one or more carbide powders on the basis of dependence of specified nanopore size on physical and chemical constants of the carbides using the relationship;

$$X = Z \cdot (1 - R) / R$$

10 where X = specified size of nanopores, nm;

$$Z = 0.65 - 0.75 \text{ nm};$$

$$R = v M_c \rho_k / M_k \rho_c$$

where M_c - molecular mass of carbon, g/mole;

15 M_k - molecular mass of carbide, g/mole;

ρ_k - density of carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule,

- heat treating the intermediate body in a medium of gaseous hydrocarbon or hydrocarbon mixtures at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons until the mass of the intermediate body has increased at least 3% thereby creating a workpiece in the form of a rigid carbonaceous skeleton,
 20 thereafter thermochemically treating the work piece in a medium of gaseous halogens to provide predetermined nanopore sizes, i.e the pores have a size less than 10 nm, a predetermined volume of nanopores, and a predetermined distribution of nanopores within
 25 the volume of the article, the carbides used forming carbons having a slot-like structure

2. A method according to Claim 1, **characterised** in that elements from III, IV, V or VI
 30 group of Mendeleyv's Periodic system are selected as carbon precursor.

3. A method according to Claims 1 or 2, **characterised** in that the formulation of carbide particle mixture is chosen in dependence of desired distribution of nanopores by sizes using the relationship;

5

$$\Psi_i = K_i \varphi_i / \sum K_i \varphi_i$$

where Ψ_i - volumetric part of nanopores with size x_i in total volume of nanopores;
 φ_i - volumetric part of i-th carbide in particle mixture;
 n - number of carbides;

10

$$K_i = 1 - v M_c \rho_{ki} / M_{ki} \rho_c$$

where M_c - molecular mass of carbon, g/mole;
 M_{ki} - molecular mass of it-h carbide, g/mole;
 ρ_{ki} - density of it-h carbide, g/ccm;
 ρ_c - density of carbon, g/ccm;
 v - number of carbon atoms in carbide molecule.

15

4. A method according to any one of Claims 1-3, **characterised** in that the intermediate body is formed with a porosity of 30-70 vol%, preferably 35-50 vol%.

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5. A method according to any one of Claims 1-4, **characterised** in that the intermediate body is formed with a porosity determined with the following relationship;

25

$$\varepsilon_0 = [1 - v_{np} / \sum K_i \varphi_i] * 100$$

where ε_0 - porosity of intermediate body, vol%;
 φ_i - volumetric part of i-th carbide in particle mixture;
 v_{np} - predetermined volumetric part of nanopores in final article;

30

$$K_i = 1 - v M_c \rho_{ki} / M_{ki} \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of it-h carbide, g/mole;

ρ_{ki} - density of it-h carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

v - number of carbon atoms in carbide molecule.

5

6. A method according to any one of Claims 1-5, **characterised** in that the treatment in a medium of gaseous hydrocarbon or hydrocarbon is carried out until the mass of the intermediate body has changed according to the following relationship;

10

$$\Delta m = Q(\varepsilon_0 - v_{tr}) / (1 - \varepsilon_0)$$

where Δm - relative change of intermediate body mass, g/g;

ε_0 - porosity of intermediate body, vol%;

v_{tr} - predetermined volumetric content of transport pores, vol%;

15

$$Q = \rho_c / \rho_{mix}$$

Where ρ_c = density of carbon, g/ccm;

ρ_{mix} = density of carbides mixture, g/ccm;

20

7. A method according to any one of Claims 1-6, **characterised** in that the intermediate body is formed by pressing.

8. A method according to any one of Claims 1-6, **characterised** in that the intermediate

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body is formed by slip casting, tape casting or slurry casting.

9. A method according to any one of Claims 1-8, **characterised** in that natural gas is used as a mixture of hydrocarbons.

30

10. A method according to Claim 9, **characterised** in that the treating in hydrocarbon medium is carried out at 750-950°C.

11. A method according to any one of Claims 1-8, **characterised** in that at least one of the hydrocarbons used during the treatment of the intermediate body in hydrocarbons medium is selected from the group of acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives.

5

12. A method according to Claim 11, **characterised** in that the treating in hydrocarbon medium is carried out at 550-1200°C.

10

13. A method according to any one of Claims 1-12, **characterised** in that the particles of carbide or carbides of which the intermediate body is formed are arranged uniformly throughout its volume.

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14. A method according to any one of Claims 1-12, **characterised** in that the particles of carbide or carbides of which the intermediate body is formed are arranged non-uniformly throughout its volume.

20

15. A method according to any one of Claims 1-14, **characterised** in that the thermochemical treatment of the workpiece is carried out in a medium of gaseous halogens, such as chlorine.

25

16. A method according to any one of Claims 1-15, **characterised** in that the thermochemical treatment of the workpiece is carried out at 350-1200°C.

17. A method according to claim 15 or 16, **characterised** in that chlorine is preferably used for the thermochemical treatment at 500-1100°C.

30

18. A porous carbon article having nanopores, i.e. pores having a size less than 10 nm, and transport pores, i.e. pores having a size greater than 100 nm, **characterised** in that the article consists of a rigid carbon skeleton in which at least 3 % of its mass consists of carbon without nanopores.

19. A porous carbon article according to Claim 18, **characterised** in that it has nanopores of at least two sizes.

20. An article according to Claim 18 or 19, **characterised** in that the the volume of nanopores is 15-50 % and the volume of transport pores is 10-55 %

5 21. An article according to Claims 18,19 or 20, **characterised** in that the nanopores are distributed uniformly throughout the volume of the article.

22. An article according to Claims 18,19 or 20, **characterised** in that the nanopores are distributed nonuniformly throughout the volume of the article.

10 23. An article according to any Claims 18- 22, **characterised** in having a specific electrical capacitance of at least 30 F/g when used as electrode material in a double electric layer capacitor.

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24. ~~An article according to Claim 20,~~
c h a r a c t e r i z e d i n having a specific electrical
capacitance of at least 30 F/g when used as electrode mate-
5 ~~rial in a double electric layer capacitor.~~

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Table 1

Ex No	Carbide mixture composition (wt%)	Total volume of pores ¹⁾ V_{tot} (cc/cc)	Nanopore volume, ²⁾ V_{np} (cc/cc)	Transport pore volume ³⁾ , V_{tr} (cc/cc)	Size of pores, calculated ⁴⁾ (nm)		Size of pores, measured ⁵⁾ (nm)	
					X_1	X_2	X_1	X_2
1	100% TiC	0,67	0,32	0,35	0,8 - 0,92		0.8	

FIG. 1

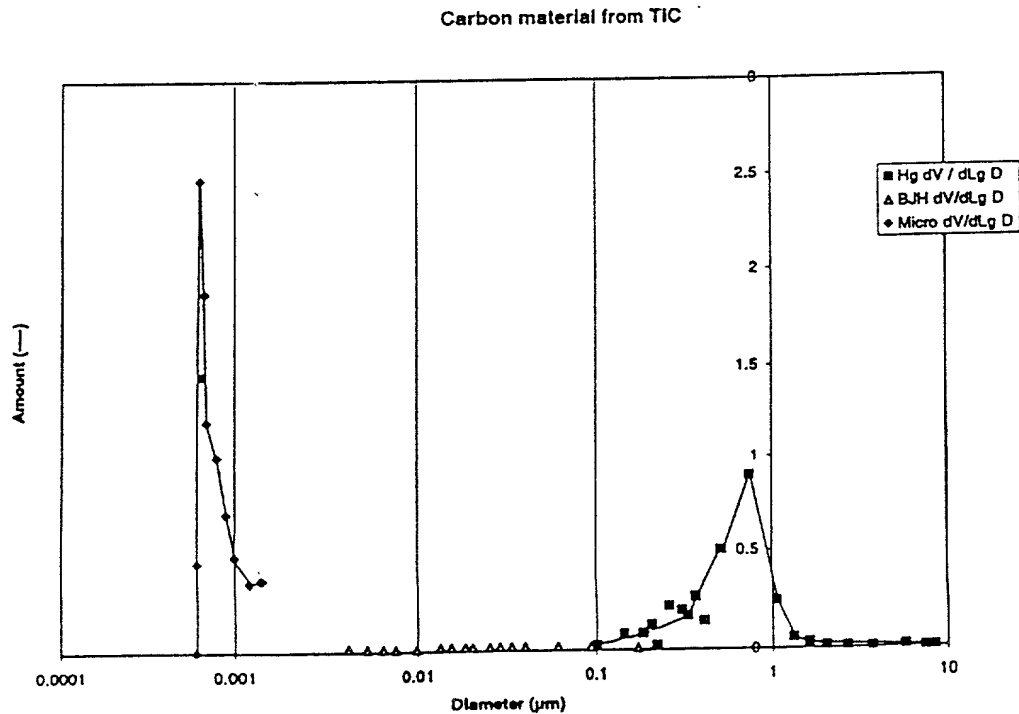


FIG. 2

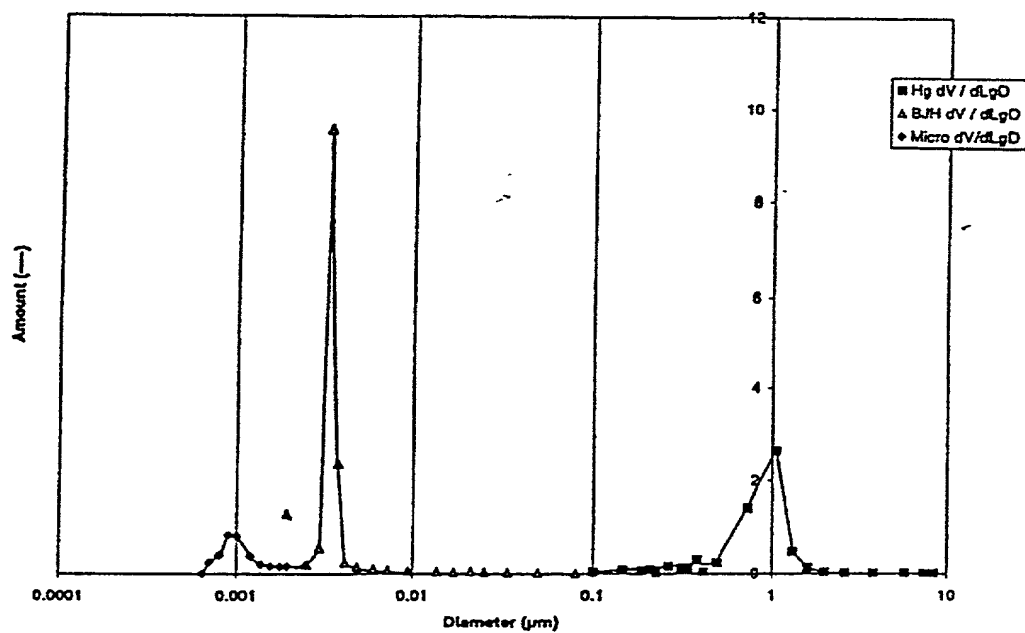
Carbon material from Mo₂C

FIG. 3

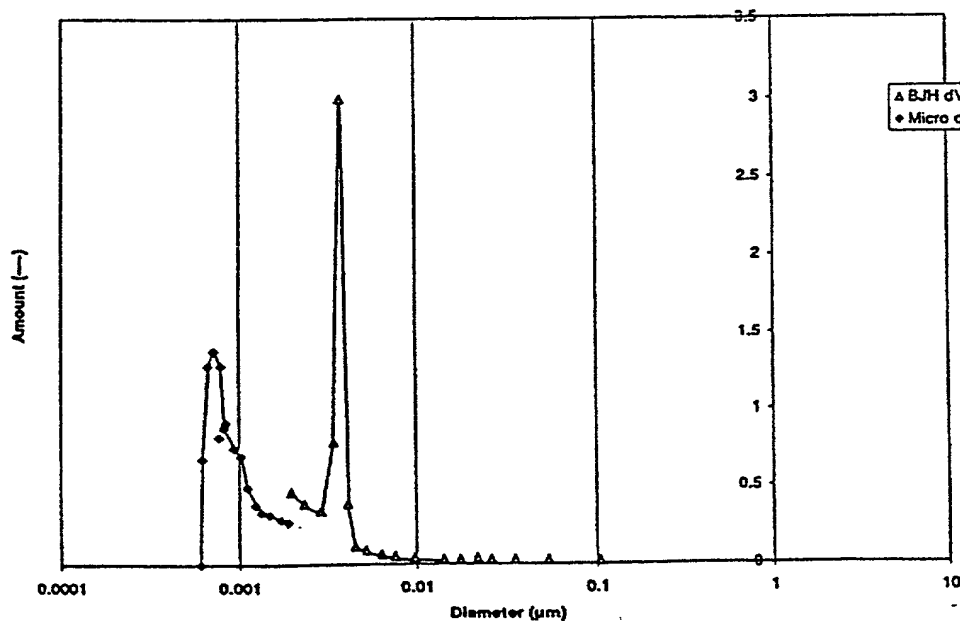
Carbon from TIC and Mo₂C

FIG. 4

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COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

- My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PRODUCING A POROUS CARBON ARTICLE AND AN ARTICLE PRODUCED THEREBY

the specification of which: *(check one)*

REGULAR OR DESIGN APPLICATION

☐ is attached hereto.

☐ was filed on _____ as application Serial No. _____
and was amended on _____ (if applicable).

PCT FILED APPLICATION ENTERING NATIONAL STAGE

☒ was described and claimed in International application No. PCT/EP98/03204 filed on 29 May 1998 and as amended on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

PRIORITY CLAIM

I hereby claim foreign priority benefits under 35 USC 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

Country	Application Number	Date of Filing (day, month, year)	Priority Claimed
Russia	97109619	30 May 1997	yes

(Complete this part only if this is a continuing application.)

I hereby claim the benefit under 35 USC 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status--patented, pending, abandoned)

POWER OF ATTORNEY

The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from Albihts Patentbyra Stockholm AB as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: **Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoît CASTEL, Reg. No. 35,041, Eric JENSEN, Reg. No. 37,855, Thomas W. PERKINS, Reg. No. 33,027, and Roland E. LONG, Jr., Reg. No. 41,949, c/o YOUNG & THOMPSON, Second Floor, 745 South 23rd Street, Arlington, Virginia 22202.**

Address all telephone calls to Young & Thompson at 703/521-2297.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: **Sergey Konstantinovitch GORDEEV**
(given name, family name)

Inventor's signature X [Signature] Date Dec 1, 1999
Residence: **St. Petersburg, Russia** RUX Citizenship: **Russian**

Post Office Address: **Apartment 27, pr. Rybatskij, 19/1
St. Petersburg 193076, Russia**

Full name of second joint inventor, if any: **Robert Gustavovitj AVARBZ**
(given name, family name)

Inventor's signature X [Signature] Date Dec 1, 1999
Residence: **St. Petersburg, Russia** RUX Citizenship: **Russian**

Post Office Address: **Apartment 23, Korolenkostreet, 7
St. Petersburg 191104, Russia**

Full name of third joint inventor, if any: **Aleksandr Efimovitj KRAVTJIK**
(given name, family name)

Inventor's signature X [Signature] Date Dec. 1, 1999
Residence: **St. Petersburg, Russia** RUX Citizenship: **Russian**

Post Office Address: **Apartment 48, Statjek prospect, 11
St. Petersburg 198097, Russia**

Full name of fourth joint inventor, if any: Julia Aleksandrovna KUKUSJKINA
(given name, family name)

Inventor's signature X Kyfn Date Dec 1, 1999

Residence: St. Petersburg, Russia RUX Citizenship: Russian

Post Office Address: Apartment 143, Bolsjeoktinskij prospect, 14
St. Petersburg 196160, Russia

Full name of fifth joint inventor, if any: Vasilij Vasilevitj SOKOLOV
(given name, family name)

Inventor's signature X Breuer Date Dec 1, 1999

Residence: St. Petersburg, Russia RUX Citizenship: Russian

Post Office Address: Apartment 25, Tjemoje Kazatjestvostreet, 8
St. Petersburg 198096, Russia

Full name of sixth joint inventor, if any: Tatjana Vasilevna MAZAEVA
(given name, family name)

Inventor's signature X Mas Date Dec 1, 1999

Residence: St. Petersburg, Russia RUX Citizenship: Russian

Post Office Address: House 2, Apartment 135,
Kosygin prospect, 30
St. Petersburg 195208, Russia

Full name of seventh joint inventor, if any: Alla GRECHINSKAYA
(given name, family name)

Inventor's signature X Druf Date Dec 1, 1999

Residence: St. Petersburg, Russia RUX Citizenship: Russian

Post Office Address: Apartment 22, Kuibushev Street, 20
St. Petersburg 19746, Russia